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Discovering Giuseppe Capogrossi: Study of the Painting Materials in Three Works of Art Stored at Galleria Nazionale (Rome)

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Received: 6 July 2020; Accepted: 13 August 2020; Published: 21 August 2020

Abstract: We present the results of a diagnostic campaign on three of Giuseppe Capogrossi's abstract paintings from the 1950s and 1960s, conserved at the National Gallery of Modern and Contemporary Art in Rome. Non-invasive investigations by reflection FT-IR spectroscopy were carried out, followed by micro-destructive laboratory analyses using Py-GC-MS, and HPLC-ESI-Q-ToF. The investigations focused on identifying the binders used for both the preparation and the pictorial layers. In two of the paintings investigated, an industrial preparation was identified based on egg yolk, mixed with other organic materials (acryl resin, oil, animal glue). The paint media include the use of both oil and alkyd paint. In one of the three paintings, the presence of a styrene-acryl resin was observed. The results show the simultaneous use of traditional and innovative materials, confirming the complexity of the period in which the artist was active, characterized by the technical experimentation of both the artists and manufacturers. The research also contributes to a better understanding of Giuseppe Capogrossi's artistic profile, from the point of view of executive techniques.

Keywords: Giuseppe Capogrossi; modern paint; FT-IR; Py-GC-MS; HPLC-MS

1. Introduction

From the end of the 19th century, and during the 20th century, the range of materials available for use by artists significantly changed, as artists' paint materials were increasingly produced on an industrial scale, as a consequence of scientific and technological advances, and the industrial revolution [1–3]. The paint ingredients and formulations used by artists were thus substantially and, in some cases, completely different from the composition of traditional artists' paint materials used until the 19th century.

In particular, in the mid-20th century, the manufacturers of artists' materials developed new and larger-scale technologies for producing paints, pigments and primers. Manufacturers and artists

experimented with different formulations and techniques, with the result that modern paints are more complex than traditional paint recipes, and are often affected by specific and not yet fully assessed conservation issues and risk factors [4,5]. Their composition includes a wider range of natural binders (e.g., oils) and synthetic binders (e.g., synthetic resins), modern pigments different from traditional ones, plus a wide range of additives such as stabilizers, emulsifiers, and plasticizers, needed to achieve specific rheological and physico-chemical proprieties required during use, stocking or production [6].

The polymer chemical industry played an important role in the evolution of modern art paint materials during the 20th century, and in particular after the Second World War, paints based on synthetic polymers started to be widely used by artists [1,6]. Alkyd paints, produced from natural oil media, were among the first synthetic paints, and became available at the beginning of the 20th century [7]. In the 1950s, in the USA, solvent acrylic colors produced by Rhom and Hass began to be sold. They were known as "Magna". Their advertising campaign presented solvent acrylic colors as "the first new paint binder after 500 years", and they were fully explored and exploited by Morris Louis and Roy Lichtenstein [1]. Solvent acrylic paint products were then gradually replaced by acrylic aqueous emulsions [2,8,9].

Today there is a growing awareness of the conservation issues affecting paintings produced in this period of exceptional technical innovation, which are significantly different from those presented by artworks produced with traditional historical paint materials.

The assessment of the composition of paint materials in modern paintings is fundamental to better understand the history of artistic techniques, the degradation phenomena [10], and the risk factors affecting modern art [11–14]. In addition, the results of analytical surveys on modern paints serve as the basis for attribution and authentication studies [15,16], and to plan restoration and preventive conservation strategies [17,18].

In this work, we investigated the paint materials in three paintings by Giuseppe Capogrossi (Figure 1): *Superficie 207* (1957), *Superficie 538* (1961) and *Superficie 553* (1965), all from Capogrossi's abstract period and conserved at the National Gallery of Modern and Contemporary Art in Rome. The three paintings were produced in the years corresponding to the start of the adoption of synthetic paints in Europe. Our analysis thus represents an exceptional opportunity to study a period of rapid evolution in paint techniques, and to investigate the technical features of Capogrossi's abstract production. The characterization of the materials in the three paintings enabled us to support the museum in evaluating the best conservation options for the artworks, for which a cleaning intervention was planned in 2019 as part of a long term conservation strategy.

Figure 1. From the left: *Superficie 207* (1957), *Superficie 538* (1961), and *Superficie 553* (1965).

Giuseppe Capogrossi (1900–1972) started his activity in the 1930s. His first paintings were figurative, and for contemporary art critics he was part of the "New Roman School". In 1950, he moved

towards abstractionism, creating his own unique ideograms, which were to become the main features of his production. Capogrossi's "signs" or "calligrams" are repeated in every possible composition and chromatic variation in his "Surfaces", for which Capogrossi became famous all over the world [19–22].

An important part of our research focused also on the characterization of the preparation layers, and especially those of industrial production. These layers have been poorly investigated until now, despite being of fundamental importance in determining the preservation given that they interact with the pictorial layers and restoration materials.

We used in situ non-invasive infrared spectroscopy [23] to extensively investigate the paint materials in different areas of the artworks using portable instrumentation, an approach previously applied at the Gallery to investigate modern artworks produced with different synthetic media [24]. Micro-destructive analyses were performed on a limited number microsamples using analytical pyrolysis coupled with gas chromatography/mass spectrometry (Py-GC-MS) and high-performance liquid chromatography/high resolution-mass spectrometry (HPLC-HRMS). Py-GC-MS allows the chemical characterization of natural or synthetic organic materials without any sample pretreatment, and it is particularly suitable for identifying synthetic polymers in modern paint samples [7,25–32].

HPLC-HRMS was used to characterize the lipid profiles of the paint samples in terms of the triglyceride (TAs) composition, thus enabling us to investigate the origin of the lipid materials based on the analysis of the acylglycerols [12,13,33,34].

Being destructive, chromatographic and mass spectrometric data could be obtained only for a few samples of paint materials collected from the edges of the paintings, in order to avoid any damage to the artworks. Nevertheless, the detailed molecular results achieved by mass-spectrometric micro-invasive analysis of these samples supported and helped the interpretation of the complex FTIR reflectance spectra, that on the other side could be collected from a high number of spots of the painted surfaces, being this spectrometric techniques fully non-invasive.

The combination of the non-invasive spectroscopic approach with the analytical methods based on mass spectrometry provided a complete picture of the chemical composition of the paint materials at a molecular level. The data collected led to a better understanding of Giuseppe Capogrossi's approach to creating his abstract paintings, as well as insights into his *modus operandi.*

2. Materials and Methods

2.1. The Paintings

Superficie 207 is painted on a 180 × 119 × 2-cm canvas. The support is made from cotton fiber on which an industrial preparation was applied (Figure 2c). On this layer, the artist painted a composition that at a later date he decided to cover, applying a new preparation layer, and painting the currently visible composition over it (Figure 2a,b).

The paint film is composed of different colored squares, on which the artist painted his iconic ideograms using black paint. The black areas look glossier than the colored background because Capogrossi applied a layer of varnish only on this area. This painting, vandalized in 1978, was then restored; during restoration, the original varnish was partially removed, and a new layer of varnish was applied.

Superficie 538 is painted on a 116 × 89 × 2-cm canvas. The support is a linen cover with a preparation that could be clearly identified as manually applied by the artist (Figure 3a), due to the non-uniform thickness, and the fact that it was not applied on the edges. The paint film is composed of a background full-bodied black layer on which several white and orange ideograms have been painted. Again it appears clear that the artist was interested in creating a contrast between the black glossy and matt drawings (Figure 3b).

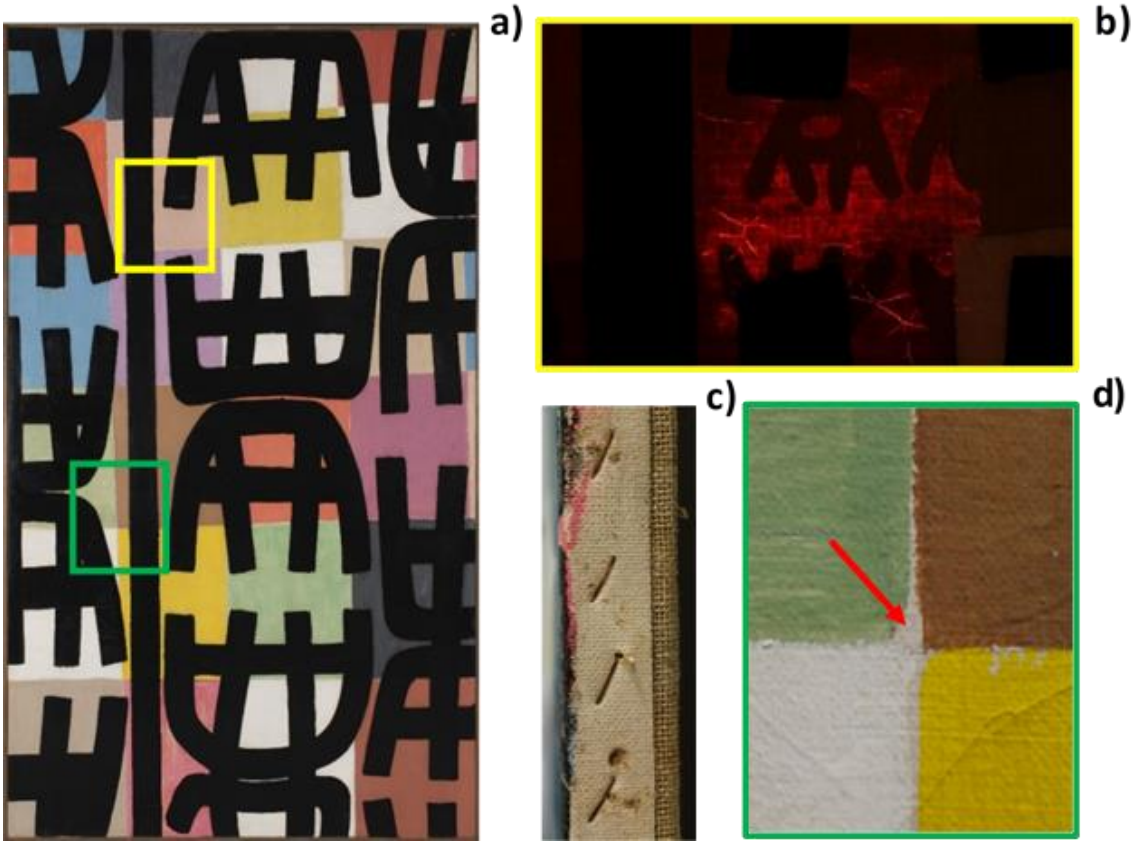

Figure 2. (**a**) *Superficie 207* with the photographic details in evidence (yellow and green square); (**b**) transillumination photo in which a previous underlayer painting is visible; (**c**) industrial preparation visible on the edge of the painting; (**d**) detail of the painted surface in which the preparation applied by Capogrossi is visible and uncovered in the center (red arrow).

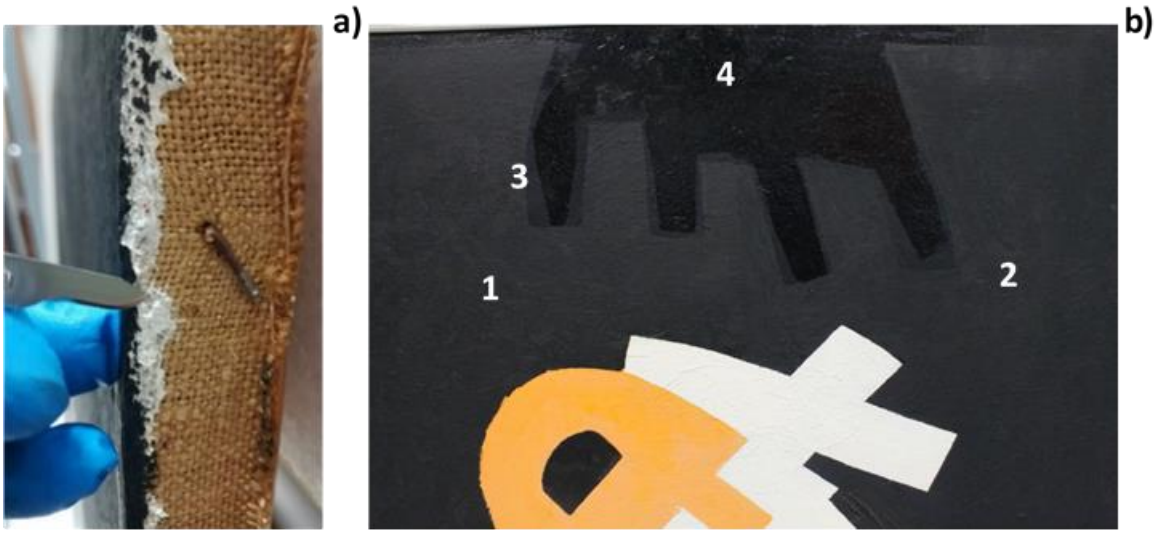

Figure 3. (**a**) Detail of the preparation layer applied by Capogrossi on the canvas of *Superficie 538*; (**b**) detail of black paints with different degrees of opacity: 1: the most opaque, 4: the most glossy.

Superficie 553 is painted on a 129 × 101 × 2-cm canvas. The support is made from cotton fiber with an industrial preparation (Figure 4a). On this already prepared canvas, Capogrossi applied a new preparation layer on which he painted the black composition and a small red area at the bottom of the painting. An additional white layer was applied contouring the black ideograms (Figure 4b).

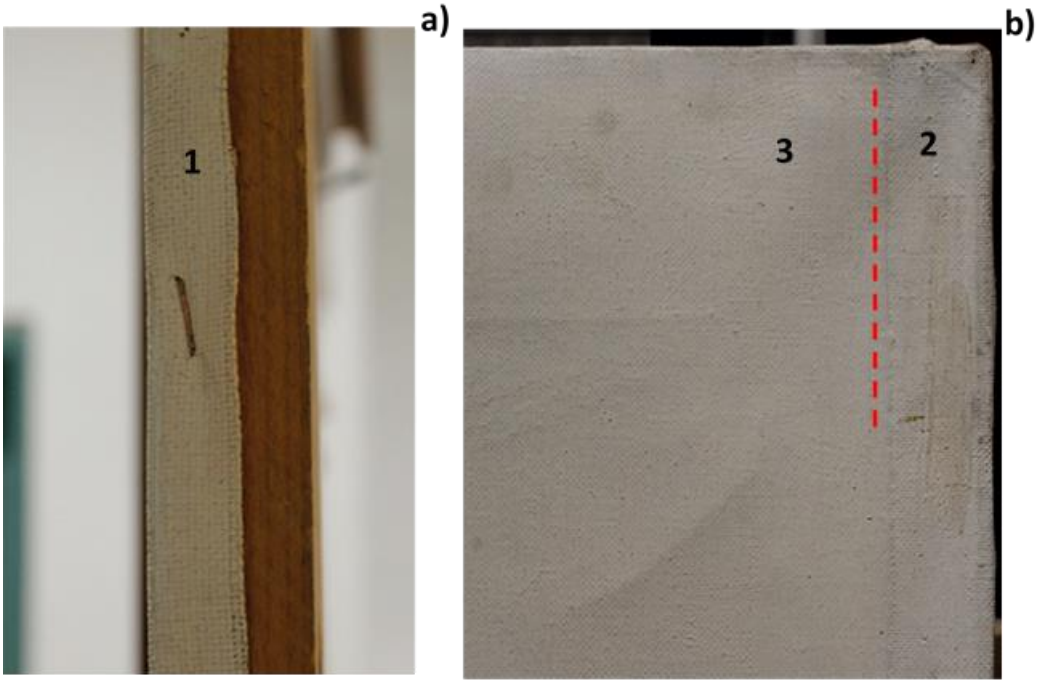

Figure 4. (**a**) Detail of the industrial preparation (1) of the *Superficie 553*; (**b**) detail of the preparation layer applied by Capogrossi (2), left visible on the surface of the painting. Capogrossi had a rethinking and reassessed the size of the painting when painting on a larger frame, leaving this area (2) exposed. On this layer, there is another white background layer (3), applied by the artist contouring the black and red composition.

2.2. Diagnostic Approach

The three paintings have been the subject of a multi-analytical diagnostic campaign carried out in the context of the research project: *Giuseppe Capogrossi's paintings at the National Gallery of Modern and Contemporary Art in Rome. Investigation on executive techniques and on the cleaning issue in modern paints*, promoted by the School of Conservation and Restoration of Cultural Heritage of the University of Urbino and the National Gallery of Modern and Contemporary Art in Rome [35,36]. The project, whose complete results will be published elsewhere in an extended form including the determination of the palette and pigments [37], involved the collaboration of several Italian institutions. It included an initial phase based on non-invasive investigations (multispectral imaging, X-ray fluorescence, reflection FT-IR spectroscopy and unilateral NMR-MOUSE [38]), followed by micro-destructive laboratory analyses (Py-GC-MS, GC/MS and HPLC-ESI-Q-ToF, SEM-EDS, optical microscopy) on the samples. Here, only the results obtained by reflection FT-IR spectroscopy, chromatography and mass spectrometry are presented, focused on the study of the organic binders in the paint and in the preparation layers.

2.2.1. Non-Invasive In Situ Reflection FT-IR Spectroscopy

We performed an initial characterization of the paint materials in the three paintings directly in situ through an extensive campaign of non-invasive FT-IR measurements (a total of 86 analysis points, see locations in Figure S1). For the infrared analysis we used a portable FT-IR spectrometer ALPHA-R produced by Bruker Optics (Ettlingen, Germany/Billerica, MA, USA). This compact spectrometer is equipped with a SiC Globar infrared source, a RockSolid™ design interferometer (a system of parabolic gold mirrors) and a room-temperature DLaTGS detector. An external reflection module with an optical layout of 22°/22° collects the infrared radiation reflected from a surface at about 1 cm of distance. The sampling areas are approximately equal to 3 mm in diameter and are visualized through an integrated USB high-resolution video camera. The reflection spectra, expressed in pseudo-absorption

units [A′ = log(1/R); R = reflection], were acquired in the spectral range from 7000 to 375 cm^{-1}, with a spectral resolution of 4 cm^{-1} and using 186 scans. Spectra from a flat gold mirror were used for the background correction.

2.2.2. Sampling for Mass Spectrometric Analysis

The criterion chosen for selecting the sampling points for microdestructive analysis was the minimal invasiveness, in order to avoid any possible damage to the painted surface. For this reason, the microsamples were collected at the edges of the paintings (Figure 5).

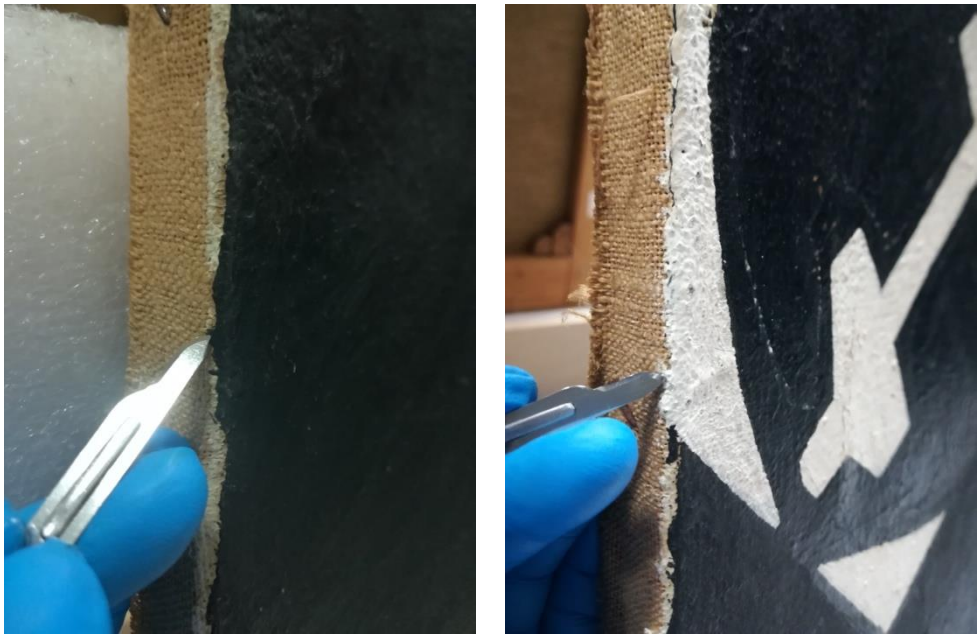

Figure 5. Sampling from *Superficie* 538.

For *Superficie 207*, eight samples were taken, one of which was the industrial preparation layer taken from the lower edge (207-industrial preparation), and seven samples were related to the paint film (207-blue, 207-fuchsia, 207-gray, 207-brown, 207-beige, 207-white, 207-black).

For *Superficie 538*, seven samples were taken, one collected from the preparatory layer applied by the artist (538-preparation), and six related to the paint film (538-white1, 538-white2, 538-glossy black1, 538-glossy black2, 538-opaque black1, 538-opaque black2).

Finally, for *Superficie 553* two samples were taken, one from the industrial preparation (553-industrial preparation) and one related to the preparation made by Capogrossi (553-2 preparation).

2.2.3. Py-GC-MS

Py-GC-MS analyses were performed using a multi-shot pyrolyzer EGA/PY-3030D (Frontier Lab, Koriyama, Japan) coupled with a 6890 N gas chromatography system with a split/splitless injection port, and combined with a 5973 mass selective single quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Pyrolysis conditions were optimized as follows: pyrolysis chamber temperature 550 °C, interface 280 °C. The GC injector temperature was 280 °C. The analyses with the derivatizing agent were performed by adding 2 µL of hexamethyldisilazane (Sigma-Aldrich, St. Louis, Missouri, US) directly into the pyrolysis cup beforehand.

The complete chromatographic and mass spectrometric conditions for both the analytical procedures are reported in [12,13,39].

2.2.4. HPLC-ESI-Q-ToF

For the HPLC analysis of TAGs, ~0.1 mg of each paint sample was subjected to microwave-assisted extraction in an Ethos One microwave oven (Milestone Srl, 24010 Sorisole, Italy) (power 600 W), with 300 µL of a chloroform-hexane (3:2) mixture at 80 °C for 25 min. The extracts were dried under a nitrogen stream, diluted with 600 µL of elution mixture, and filtered on a 0.45 µm PTFE filter (Grace Davison Discovery Sciences, Columbia, Maryland, USA) just before injection [12]. All the solvents used for the extraction were HPLC-MS grade (Sigma-Aldrich).

All the analyses were carried out on a 1200 Infinity HPLC coupled by a Jet Stream ESI interface with a Quadrupole-Time of Flight tandem mass spectrometer 6530 Infinity Q-ToF detector (Agilent Technologies, Santa Clara, CA, USA). The chromatographic separation was performed on an Agilent Poroshell 120 EC-C18 column (3.0 mm × 50 mm, 2.7 µm) with a Zorbax eclipse plus C-18 guard column (4.6 mm × 12.5 mm, 5 µm). The injection volume was 2 µL and the column temperature was 45 °C. The detailed instrumental parameters for the chromatographic separation and the mass spectrometric detection and identification of the TAGs are reported in [25,26,34,40]. All the eluents used for the HPLC analyses were HPLM-MS grade (Sigma-Aldrich). Abbreviation list: P: palmitic acid, L: linoleic acid; O: oleic acid; S: stearic acid.

3. Results

3.1. Superficie 207

Non-invasive FT-IR analyses performed along the non-painted edge of the painting *Superficie 207* enabled us to characterize the preparation materials. Two different uncovered preparation layers were visible on different areas of the edge, namely the industrial preparation applied directly onto the canvas and a preparation layer applied by Capogrossi himself over the industrial pre-made preparation. In the spectrum collected from the industrial preparation (Figure 6a), we identified the marker bands of hydrocerussite [$2PbCO_3 \cdot Pb(OH)_2$] (reference spectrum in black), probably mixed with a proteinaceous and/or a lipid material. Concerning the nature of the binder, a protein component can be hypothesized on the basis of the band at ca. 1550 cm^{-1} (amide II [41,42]), while the shape of the CH *stretching* bands at ca. 2943 and 2857 cm^{-1} is more similar to that of a lipid material. However, the clear distinction of the carbonyl *stretching* mode (1740–1730 cm^{-1}) of a possible lipid component, is hampered by the spectral overlapping in the same region with the hydrocerussite signal at ca. 1740 cm^{-1} [$\nu_1 + \nu_4$ (CO_3^{2-})] [40]. These hypotheses have been evaluated at the light of the results obtained by Py-GC-MS.

In the spectrum collected from the preparation layer applied by Capogrossi, the carbonyl band along with the weak C-O *stretching* band at ca. 1155 cm^{-1} [42] (Figure 6a) suggest the presence of a possible acrylic binder mixed with titanium white. This latter, confirmed by XRF analysis described elsewhere [37], was highlighted by the characteristic spectral features (bands at ca. 750 and 550 cm^{-1} indicated in Figure 6a) of the Ti-O lattice [43].

The Py-GC-MS analyses performed on the industrial preparation sample (Figure 6b) revealed indeed the presence of an acrylic resin. This was specifically identified as an ethyl acrylate (EA) based acryl polymer, due to the presence of the monomer EA in the GC chromatogram, released by thermally induced unzipping of the polymer during pyrolysis [44].

One of the advantages of analytical pyrolysis coupled with GCMS is the possibility to identify several organic materials in one analytical run. In this case the hypothesis of the presence of egg—on the basis of the FT-IR spectra—was confirmed through the identification of the pyrolysis markers of egg yolk: hexadecanonitrile and octadecanonitrile [45] (Figure 6b). Moreover, the analysis reveals also the presence of a series of aliphatic hydrocarbons ascribable to a paraffin wax [46] (Figure 6b).

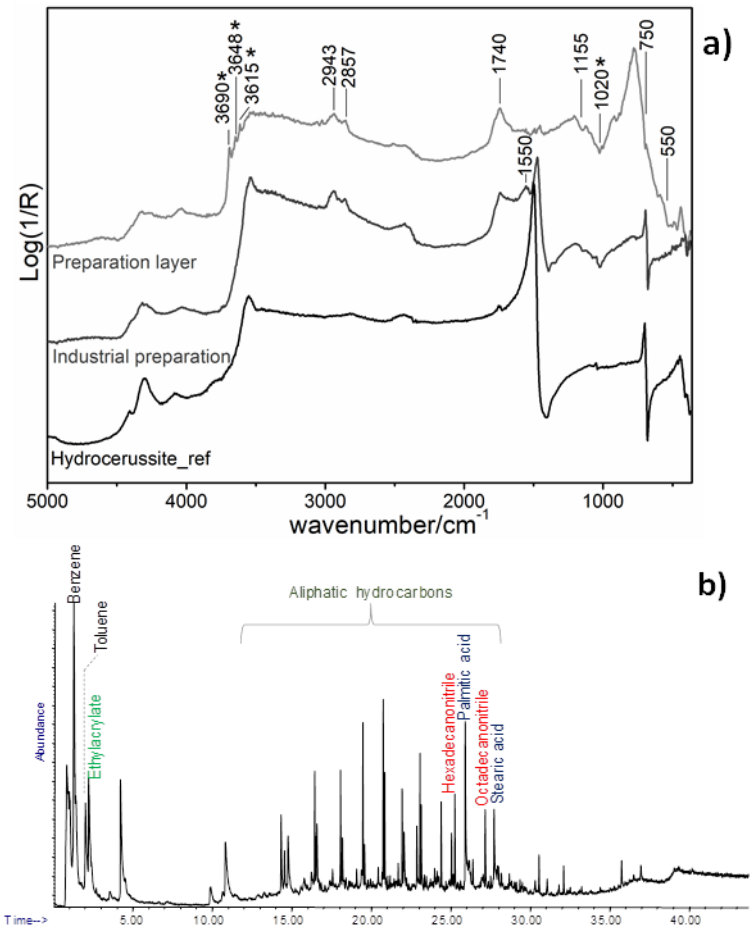

Figure 6. (**a**) Reflection mode FT-IR spectra of the two preparation layers of *Superficie 207* in comparison with a reference spectrum of hydrocerussite (kaolinite bands are marked with *); (**b**) Py-GC-MS chromatogram obtained for the industrial preparation sample of Superficie 207.

The FT-IR spectra collected from the various colored areas on the surface of *Superficie 207*, highlighted the presence of different materials. In most of the examination spots, the presence of an acrylic resin (marker bands at ca. 1740 and 1155 cm^{-1}, Figure 7a) can be hypothesized though a spectral overlapping with the sulphates of the pigment formulations (i.e., gypsum, barium sulphate and/or lithopone) complicated its identification (Figure 7a). In addition, the bands in the NIR range between 4700–4500 cm^{-1} suggested a styrene component [47], probably associated with the formulation of the acrylic resin (the comparison with a reference spectrum of a Sty/n-BA copolymer is shown in Figure 7a). Exclusively in two reflection FT-IR spectra collected from a beige area (M_29 and M_30 in Figure S1a), on the other hand, the detection of the bands at ca. 1260 (C-O-C *stretching*), 1375 and 1435 cm^{-1} (CH *bendings*), along with the carbonyl *stretching* mode at ca. 1738 cm^{-1}, revealed a vinyl resin (Figure S3) in mixture with titanium white (band at ca. 750 cm^{-1}). XRF showed that this spot is rich in titanium and zinc (results published elsewhere [37]. Although Capogrossi frequently used vinyl resins as a paint binder [35], the vinyl may have been applied in a later conservation treatment. In most of the spectra acquired, infrared marker bands of zinc oxalates at ca. 1320 and 1364 cm^{-1} (C-O *stretching*) [48] and zinc carboxylates at ca. 1540 cm^{-1} (COO^{-} *stretching*) [49] were also detected (Figure 7a).

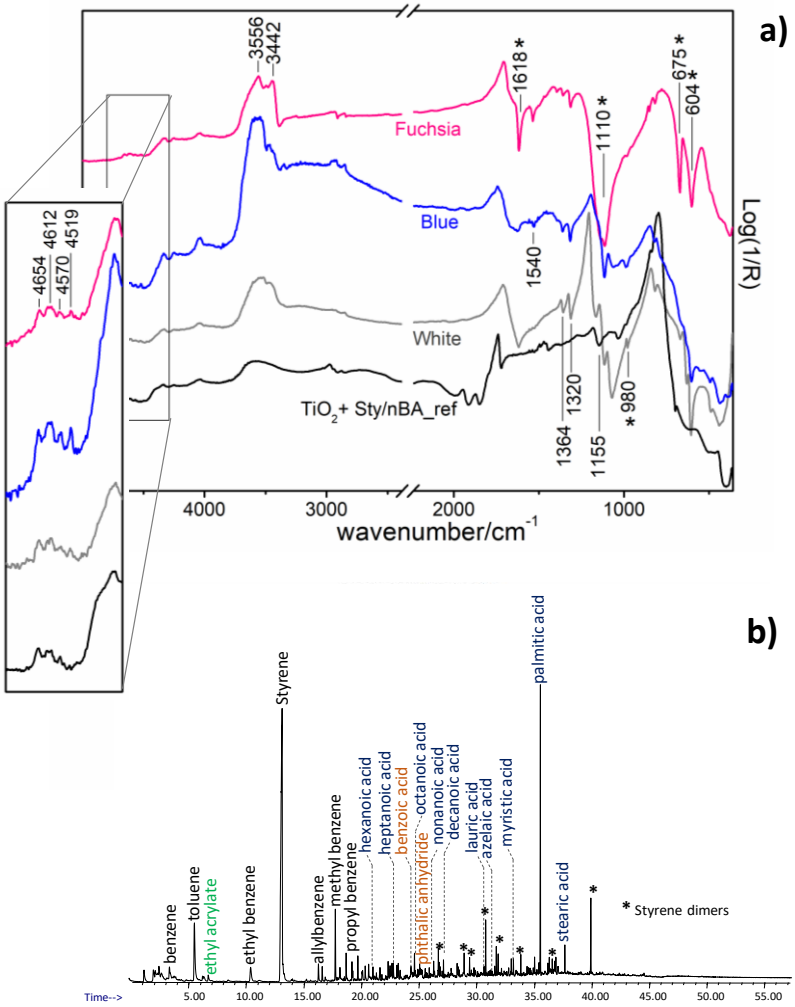

Figure 7. (**a**) Reflection mode FT-IR spectra of white, blue and fuchsia areas of *Superficie 207* in comparison with a reference spectrum of titanium white mixed with a styrene/n-butyl acrylate (Sty/n-BA) copolymer (sulphate bands are marked with *); (**b**) Py-GC-MS chromatogram obtained for sample 207-fuchsia from *Superficie 207*, showing the presence of the pyrolysis markers of both alkyd and acryl resins.

The IR measurements performed on the black ideograms indicated the use of ivory black (phosphate group bands at ca. 1038 and 604 cm^{-1} and marker signal at ca. 2010 cm^{-1} [50], Figure S4) as a pigment and of a lipid-based medium (CH *stretching* bands at ca. 2916 and 2842 cm^{-1} and carbonyl band at ca. 1740 cm^{-1}). However, in most of the black areas, the identification of the lipid compound was hampered by the presence of bands derived from an acryl polymer (spectral features at ca. 1740 and 1155 cm^{-1} indicated in Figure S4). The bands attributed to an acryl polymer were not evident for three (M_32, M_33 and M_37, see Figures S1a and S4) of the eight black spots examined. In these spectra ester and CH bonds were observed, which would seem to indicate a lipid media. The non-homogeneity of the acryl materials, and the fact that their intensity decreased significantly after the cleaning tests [35], suggest that the acryl material is a varnish layer present on the black areas as a finishing layer. Further confirmation of the nature of the varnish and of the lipid paint media was achieved by Py-GC-MS analysis of the bulk of the paint layer.

The Py-GC-MS analyses performed on the colored sections of *Superficie 207* (samples 207-blue, 207-fuchsia, 207-gray, 207-brown, 207-beige, 207-white, 207-black) showed the presence of series of fatty acids (C_6-C_{18}) and dicarboxylic acids, with azelaic acid as the most abundant, which highlighted the presence of an oxidized lipid material [12]. In addition, the presence of benzoic acid and phthalic anhydride in the profiles indicates that the lipid material is an alkyd resin based paint [7,27] which

was not recognized by non-invasive FT-IR spectroscopy due to the fact that the characteristic alkyd bands at ca. 1270 (C–O–C *stretching*), 1132 (C–O *stretching*) and 1079 cm^{-1} (C–C *bending*) [42] were not clearly observed. Figure 7b reports the Py-GC-MS chromatogram obtained for sample 207-fuchsia, and Figure 8 the one obtained for the sample 207-black. The pyrolysis profiles related to the other samples from *Superficie 207* are included in the Supplementary Material (Figure S5). Some of the pyrolysis profiles featured the markers of an acryl resin (EA, ethylacrylate) and styrene resins detected by the infrared spectroscopy analyses [26,44], suggesting that a solvent acryl paint had been mixed with the alkyd paint.

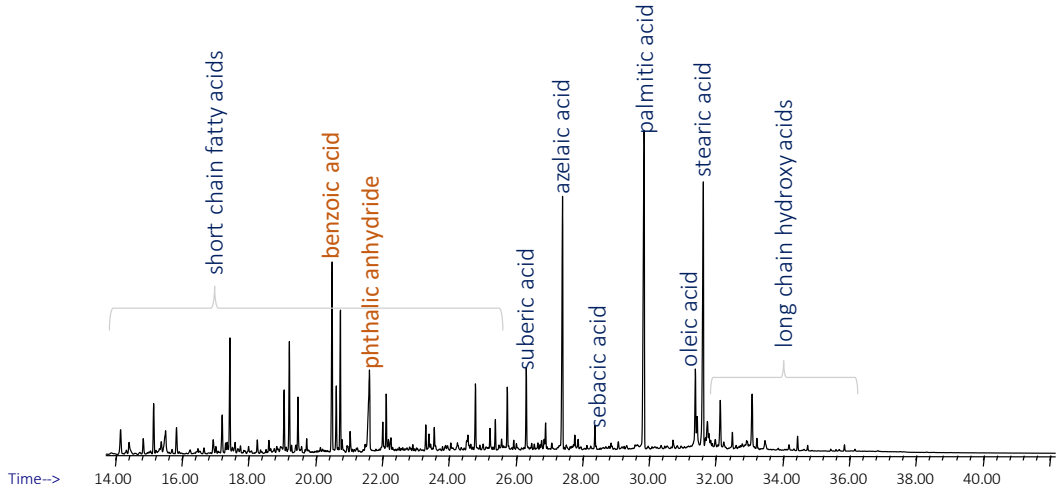

Figure 8. Py-GC-MS chromatogram obtained for sample 207-black from *Superficie 207* showing the typical pyrolysis profile of an alkyd paint.

3.2. *Superficie 538*

In the preparation layer applied by Capogrossi on *Superficie 538*, gypsum mixed with a proteinaceous material was detected by non-invasive FT-IR spectroscopy (data not shown). The Py-GC-MS analyses carried out on the preparation sample (538-preparation), enabled us to characterize the proteinaceous material as animal glue by the identification of pyrrole, 2-methyl-pyrrole and diketopiperazines, characteristic pyrolysis markers of collagen [34,51].

The infrared measurements performed on white (mixture of titanium and zinc white as confirmed by XRF data [37]) and orange paints (representative spectra are shown in Figure 9a) indicated the use of an oil medium (CH combination bands at ca. 4330 and 4260 cm^{-1} are visible in addition to CH and C=O *stretching* bands [42]). This was also confirmed by the detection of sharp inverted bands at ca. 1540, 1460, and 1400 cm^{-1} ascribable to zinc soaps of saturated long chain fatty acids (i.e., stearic acid and/or palmitic acid) [48]. In most of the spectra acquired from both the glossy and the opaque black areas, very sharp CH *stretching* and *bending* bands at about 3000 and 1460 cm^{-1}, respectively, in combination with the doublet at ca. 730 and 720 cm^{-1} due to CH_2 rocking vibration, revealed the presence of a material containing long chain aliphatic hydrocarbons such as beeswax or paraffin (Figure 9b) [52]. Moreover, exclusively in some opaque blacks, spectral features ascribable to calcium carbonate were detected. The IR carbonate (CO_3^{-2}) bands at ca. 1410 (ν_3), 875 (ν_2), 1796 ($\nu_1 + \nu_4$) and 2510 ($\nu_1 + \nu_3$) cm^{-1} [53] are indicated with C in Figure 9b.

Chromatographic analysis of the paint confirmed the use of an oil media, and the absence of phthalic anhydride and benzoic acid ruled out the presence of an alkyd resin.

In order to identify the lipid binder used by the artist, two samples, 538-glossy black-1 and 538-white-1, were analyzed by HPLC-MS in order to gain a more thorough characterization of their lipid profiles. The black sample (Figure 10) was characterized by the presence of the following triglycerides (TAGs): LLL (*m/z* 901.7, $[M + Na]^+$), OOL (*m/z* 905.8, $[M + Na]^+$), PLP (*m/z* 853.7, $[M + Na]^+$), OOP (*m/z* 881.8, $[M + Na]^+$), OOO (*m/z* 907.8, $[M + Na]^+$), OSP (*m/z* 901.8, $[M + Na]^+$), PSP (*m/z* 857.7, $[M + Na]^+$),

OOS (*m*/*z* 909.8, $[M + Na]^+$), OSS (*m*/*z* 911.8, $[M + Na]^+$), SSS (*m*/*z* 913.8, $[M + Na]^+$), and several high molecular weight TAGs containing behenic, lignoceric, and arachidic acids as acyl substituents. This lipid profile, together with the presence of oxidized species associated with the oxidation of TAGs containing linoleic and linolenic acids as acyl substituents, indicated that the paint used by the artist contained safflower oil [25,26], a semi-siccative oil indicated mostly for light colors thanks to its less tendency to yellow [54].

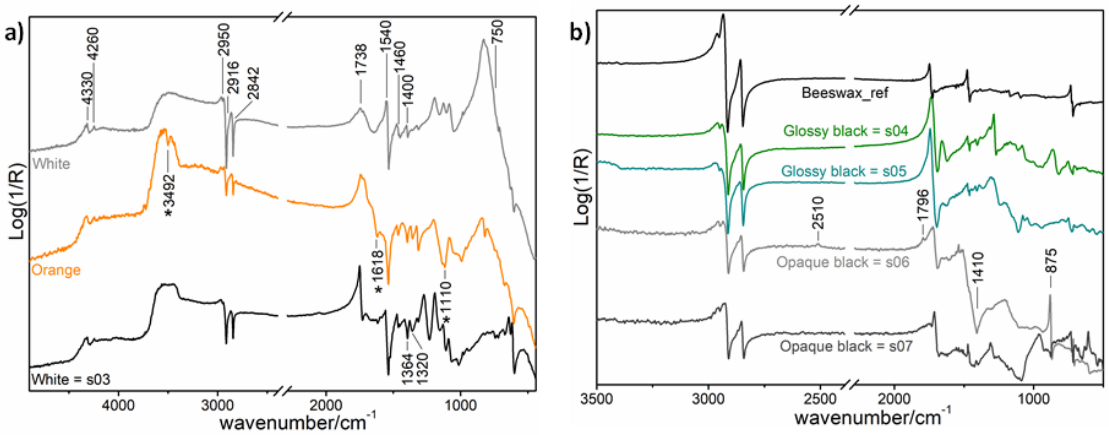

Figure 9. (**a**) Representative reflection mode FT-IR spectra of white and orange areas of *Superficie 538* (gypsum bands are marked with *); (**b**) reflection mode FT-IR spectra of glossy and opaque black areas of *Superficie 538* corresponding to sampling points s04, s05, s06 and s07, in comparison with a reference spectrum of beeswax.

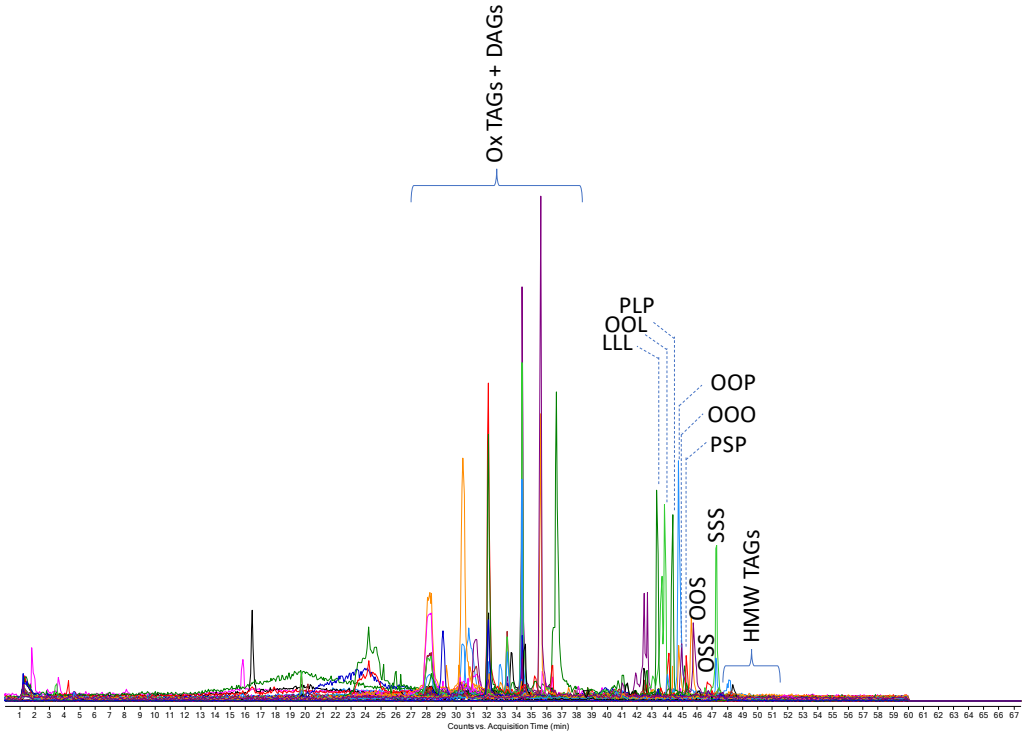

Figure 10. HPLC-MS extracted ion current chromatograms obtained in positive ionization mode for the extracts of the 538-glossy black-1 sample from *Superficie 538*; Abbreviation list: P: palmitic acid, L: linoleic acid; O: oleic acid; S: stearic acid.

The white sample (Supplementary Materials) was characterized by a higher oxidation degree, highlighted by the absence of TAGs containing polyunsaturated acyl substituents, such as linolenic acid,

and the presence of lower abundances of oxidized TAGs [55]. The lipid profile was mainly characterized by the presence of PLP (*m*/*z* 853.7, $[M + Na]^+$), OOO (*m*/*z* 907.8, $[M + Na]^+$), OSP (*m*/*z* 901.8, $[M + Na]^+$), SSS (*m*/*z* 913.8, $[M + Na]^+$) and high molecular weight TAGs. These results, in agreement with those obtained for the black sample, suggested also in this case a modern oil paint based on safflower oil, an ingredient of industrial oil paint introduced since the end of 19th century [25,26,56].

3.3. *Superficie 553*

Non-invasive FT-IR investigations performed on *Superficie 553* revealed the use of an oil binder in both the preparation applied by Capogrossi and in the paint layer (Figure 11). In the background, XRF data revealed the presence of a mixture of titanium and zinc white, while in the FT-IR spectra the characteristic spectral features of both zinc oxalates and carboxylates were recognized. In line with the results obtained for *Superficie 538*, also in the black areas of this painting a wax-like material was detected (see the comparison with a beeswax reference spectrum in Figure 11b). The phosphate group bands at ca. 1038 $\nu_3(PO_4^{3-})$, 604 and 567 $\nu_4(PO_4^{3-})$ and the signal at ca. 2010 cm^{-1} indicated that the black pigment was ivory black [50], probably mixed with Prussian blue, which was evident from the weak CN *stretching* band at ca. 2097 cm^{-1} [57]. The presence of black ivory and Prussian blue was confirmed by XFR analyzes which revealed the presence of calcium and iron [37].

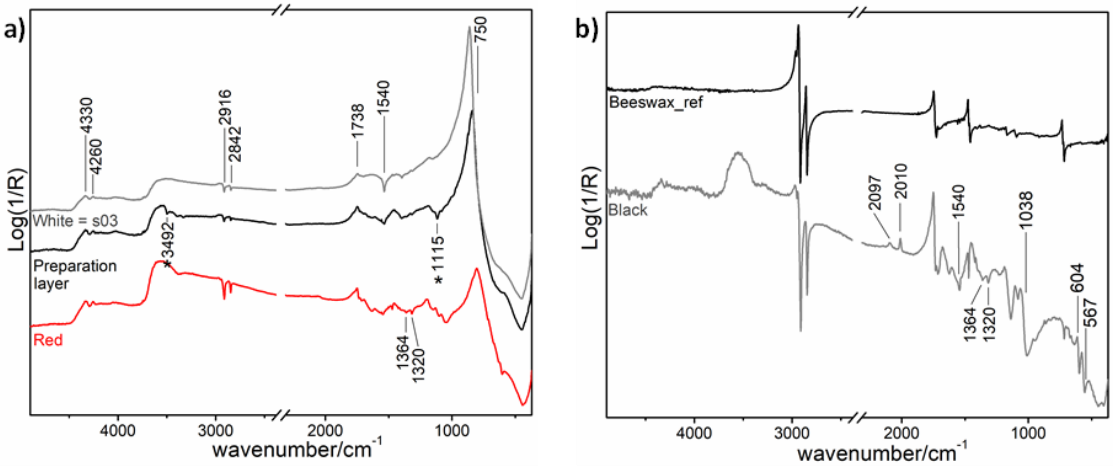

Figure 11. (**a**) Representative reflection mode FT-IR spectra of the preparation applied by Capogrossi (black line), white (spectrum collected from sampling point 3 indicated with grey line) and red areas of *Superficie 553* (gypsum bands are marked with *); (**b**) representative reflection mode FT-IR spectrum of the black areas of *Superficie 553* in comparison with a reference spectrum of beeswax.

The Py-GC-MS profile obtained for the industrial preparation sample (Figure 12) was characterized by the presence of pyrrole and diketopiperazines, suggesting also in this case the presence of animal glue [51]. The analyses also showed the presence of a significant amount of fatty acids, together with a limited amount of dicarboxylic acids, also suggesting the presence of oil. Finally, the Py-GC-MS analysis revealed hexadecanonitrile and octadecanonitrile, which are both molecular markers characteristic of egg yolk [58].

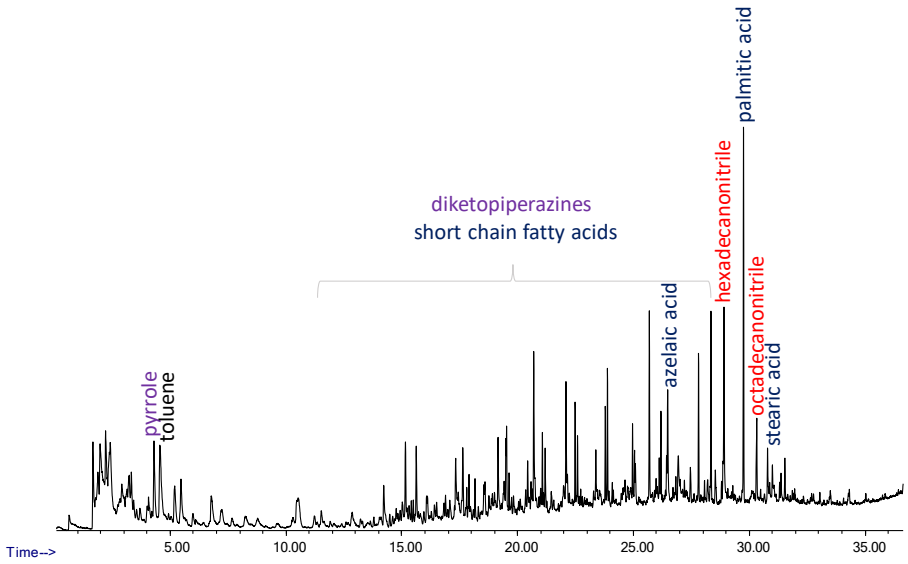

Figure 12. Py-GC-MS chromatogram obtained for the industrial preparation sample of *Superficie 533*.

4. Discussion

The collected data provided important information on the presence of specific and unexpected organic materials in the preparation and the paint layer of the *Superfici*.

The data obtained from the analyses of the industrial preparations of *Superficie 207* and *Superficie 553* showed that the manufacturers of the time used complex formulations that still included traditional materials. The common element found in the industrial preparation layers of the two artworks was egg yolk, which was used as a paint binder in traditional paintings, but not for the preparation layers (except for egg white which was very occasionally used as a priming layer). The use of egg yolk in the preparation, has been directly confirmed by artists, such as Giorgio De Chirico, for example, who in his "Piccolo trattato di tecnica pittorica" ("Small Treatise on Painting Technique") [59], reports that he used egg as a primer to make the preparation less absorbent to the binder and to enable to brush to slide easily on the surface.

The presence of acryl resin in the industrial preparation of *Superficie 207* is interesting. In Europe, the first acrylics in aqueous dispersion paints were already on the market when the artwork was produced, and in particular, the use of acrylic dispersions in Italy is documented from 1963 [60]. The fact that, in 1957, when the painting was executed, Capogrossi already had a canvas for painting with acrylic binders available is evidence of how, by the end of the 1950s in Italy, these new pictorial materials had already begun to be diffused.

The use of acryl resins for the industrial preparations is indeed mentioned in later sources, as in the Ray Smith artist's manual, which refers to "acrylic plaster based mestics" [60]. These were in fact not composed of plaster, but of pigmented acryl dispersions, erroneously named plaster or mestic. They were considered an improvement to traditional materials, and capable to ensure greater elasticity and stability in the preparatory layer. Smith's manual was published in 1988, and therefore later than when Capogrossi was active, however it demonstrates how acrylic resins, at least at the end of the 1980s, were widely used not only as a pictorial medium, but also as a binder for preparations. In fact, Smith reports that the acryl preparations were specifically formulated to paint with acrylic colors, and not recommended for oil painting on canvas due to the different mechanical properties of the two media.

For what concerns the identification of the paint binder, our analysis highlighted that the medium used in the paint binders of *Superficie 538* and *Superficie 553* was an oil binder. Capogrossi was an expert in oil binders, which he widely exploited during his figurative period [61]. One of the brands of

oil color used by Capogrossi was the "Rembrandt", which he referred to in a letter in 1962, addressed to the Musée Royaux des Beaux-Arts (Belgium) and preserved at the Capogrossi Foundation at Rome [35].

Superficie 538, also presents some interesting technical features: the aim of the artist was to organize the space by switching between glossy and opaque areas. For the opaque areas, he likely added wax or paraffin to the color mixture to achieve opacity. Our identification of calcium carbonate suggested that Capogrossi probably used this additive to obtain an even more opaque and full-bodied paint layer. Several art technique manuals of the period describe the use of calcium carbonate to obtain this effect [62,63].

Superficie 207 is very different from the other two paintings analyzed, because in this case Capogrossi used styrene-acrylic and alkyd paints as binders [5]. The background of the painting was created by mixing alkyd and styrene-acrylic resins, while for the black areas, he used only alkyd resin. The mixture of different resins was thus deliberate.

As regards the acrylic varnish identified by the FT-IR only in the black areas, the archival research relating to the restoration works after the vandalisation showed that the original varnish was regenerated with turpentine essence, and re-varnished with a commercial retouching varnish based on acrylic resin. The styrene found in *Superficie 207*, which is still widely used today, was often added as a substitute or additive for acryl resins, thus saving on production costs [5].

5. Conclusions

The combined use of non-invasive and micro-destructive analyses enabled us to obtain a complete overview of all the organic materials used in the three Capogrossi paintings. In particular, the molecular analysis carried out on a few microsamples by chromatographic techniques coupled with mass spectrometry supported the interpretation of the complex reflection mode FT-IR spectra. On the other side, the complete non-invasiveness of reflection FT-IR spectroscopy allowed us to gain information, using this technique, on a consistent number of representative spots of the paint surface of the three artworks, achieving the possibility to extrapolate the PY-GC-MS results also to area of the paintings where it was not possible to take samples. The results are summarized in Tables 1–3 and briefly:

- *Superficie 207* (1957): egg yolk and hydrocerussite were identified in the industrial preparation mixed with acrylic resin and paraffin, while titanium white and styrene-acrylic resin were used for the preparation applied by Capogrossi. The background was created using a mixture of alkyd and styrene-acrylic resin, while for the black ideograms only an alkyd binder was used. In addition, on the black ideograms, a varnish layer based on acrylic resin was detected;
- *Superficie 538* (1961): a mixture of gypsum and animal glue was identified in the preparation applied by Capogrossi, while a combination of safflower oil and wax was used in the paint;
- *Superficie 533* (1965): an industrial preparation based on animal glue, oil and egg yolk was identified; the preparation layer applied by Capogrossi was based on zinc and titanium white in the oil binder and a pictorial film based on oil. The black ideograms were created with ivory black mixed with Prussian blue and beeswax or paraffin.

This study enabled us to study Capogrossi's executive techniques and to reveal the complexity of the examined historical period in terms of both the paint materials and techniques.

The scientific analyses highlighted how Capogrossi was at the forefront of experimentation with new paint binders, using not only oil media but also alkyd and acrylic binders.

Table 1. *Superficie 207*: summary of the obtained results and identified materials.

Samples or Analysed Areas	Py GC/MS Results	FT-IR Results	Elemental Analysis [57]	Identified Materials
Preparation layers:				
Industrial preparation	Ethylacrylate based acryl polymer; egg yolk, paraffin wax	Hydrocerussite [$2PbCO_3{\cdot}Pb(OH)_2$] probably mixed with a proteinaceous and/or a lipid material	SEM-EDS: Pb	Acryl resin, egg yolk and paraffin
Preparation applied by Capogrossi	-	Possible acryl resinin mixture with titanium white	SEM-EDS: Ti XRF: Ti, Zn	Acryl resin, titanium white
Pictorial Layers:				
Colored squares of the background	Acryl resin (ethylacrylate) and styrene resins; alkyd resin	Acryl resin; styrene component	-	Acryl resin in mixture with alkyd resin
Black areas	Alkyd resin	Lipid-based medium; ivory black	SEM-EDS: Ca XRF: Fe, Ca	Alkyd resin with ivory black
Varnish on the Black Areas				
	-	Acryl resin	-	Only on the black ideograms: a varnish layer based on acryl resin applied by the artist and restoration varnish applied after the vandalization

Table 2. *Superficie 538*: summary of the obtained results and identified materials.

Samples or Analyzed Areas	HPLC-MS	Py GC/MS Results	FT-IR Results	Elemental Analysis [57]	Identified Materials
Preparation Layers:					
Preparation applied by Capogrossi	-	Animal glue (pyrrole, 2-methyl-pyrrole and diketopiperazines)	Gypsum in mixture with a proteinaceous material	XRF: Ca	Gypsum and animal glue
Pictorial Layers:					
Opaque black areas	-	Oil medium	Oil medium; beeswax or paraffin; calcium carbonate	XRF: Ca	Oil medium, beeswax or paraffin and calcium carbonate.
Glossy black areas	Safflower oil	Oil medium	Oil medium; beeswax or paraffin; calcium carbonate		Oil medium (safflower oil) and beeswax or paraffin.
Orange area	-	-	Oil medium	-	Oil medium
White area	Safflower oil	Oil medium	Titanium and zinc white; oil medium	XRF: Zn, Ti	Titanium and zinc white in oil medium (safflower oil)

Table 3. *Superficie 533*: summary of the obtained results and identified materials.

Samples or Analyzed Areas	Py GC/MS Results	FT-IR Results	Elemental Analysis [57]	Identified Materials
Preparation layers:				
Industrial preparation	Animal glue and oil medium	-	-	Animal glue, oil medium and egg yolk
Preparation applied by Capogrossi	-	Oil medium	XRF: Zn, Ti	Zinc and titanium white in oil medium
Pictorial layers:				
White area (background)	-	Oil medium; titanium and zinc white	XRF: Zn, Ti	Zinc and titanium white in oil medium
Black area	-	Oil medium; beeswax and ivory black in mixture with Prussian blue	XRF: Ca, Fe	Ivory black in mixture with Prussian blue in oil medium and beeswax
Red area	-	Oil medium; beeswax	-	Oil medium and beeswax

Finally, the results obtained in this study will be used to define the best restoration/cleaning approaches for the restoration campaign of the artworks. The conservation of *Superficie 553* has been already carried out at the moment of the publication of this article, and it consisted of a complex cleaning operation, which allowed the removal of the layer of dirt on the painting surface. The cleaning approach took into account the issues related to the unvarnished and relatively young oil paint surface [35,37]. The cleaning tests were carried out using different methods, from dry cleaning to the aqueous environment and polymeric macro-emulsions, monitoring the surface through scientific investigations, which helped to establish the best cleaning method for that surface [64–66].

Supplementary Materials: The following are available online at http://www.mdpi.com/2571-9408/3/3/52/s1.

Author Contributions: Conceptualization, D.D.L., P.C., C.M., M.P.C., J.L.N., F.M.; methodology: D.D.L., P.C., C.M., E.M., P.M., J.L.N., F.M.; validation: D.D.L., P.C., C.M., E.M., P.M., J.L.N., F.M.; investigation: P.M., J.L.N., S.P., E.M.; resources: D.D.L., P.C., M.P.C., C.M., F.M.; writing—original draft preparation: E.M., P.M., J.L.N.; writing—review and editing: all authors; funding acquisition: D.D.L., P.C., C.M. All authors have read and agreed to the published version of the manuscript.

Funding: The diagnostic campaign was partly supported by MIUR through the National Access call (E-RISH.it, http://www.e-rish.it) within the European Research Infrastructure for Heritage Science funded by the European Commission (H2020 INFRADEV-2016-2, GA n. 739503).

Acknowledgments: The authors acknowledge all the institutions and scientists involved in the interdisciplinary project and in particular Maria Pia Sammartino from the Chemistry and Physics Department of University of Rome "La Sapienza"; Marcello Colapietro, and Ombretta Tarquini from the Crystallography Institute of CNR of Rome; Noemi Proietti and Valeria di Tullio from the Institute of Chemical Methodologies of CNR of Rome. Cristiana Collu: Director of National Gallery of Modern and Contemporary Art (Rome) and Laura Baratin, President of the School of Conservation and Restoration of Cultural Heritage of the University of Urbino "Carlo Bo", are gratefully acknowledged for making the research project possible. Cristiana Collu and the National Gallery of Modern and Contemporary Art (Rome) are also thanked for hosting all the partners of the project. The authors are grateful to Guglielmo Capogrossi Guarna, President of the Fondazione Archivio Capogrossi, Rome, for the support given to the research. The institutions and people responsible for the project are: University of Urbino Carlo Bo, Department of Pure and Applied Sciences, working group: Laura Baratin, Daphne de Luca, Paolo Triolo, Sara Barcelli; National Gallery of Modern and Contemporary Art in Rome, working group: Cristiana Collu, Paola Carnazza, Massimo Mininni; consultant: Tommaso Strinati. J. La Nasa, F. Modugno and S. Pizzimenti are grateful to Ilaria Bonaduce (Department of Chemistry and Industrial Chemistry of University of Pisa) for the fruitful discussions on the analytical strategy to be adopted.

Conflicts of Interest: The authors declare no conflict of interest.

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